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# PATENT SPECIFICATION

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(19)

## (54) METHOD OF MAKING A NOVEL STARCH DERIVATIVE AND THE PRODUCT PRODUCED THEREBY

(71) We, NATIONAL STARCH & CHEMICAL CORPORATION, a Company organized and existing under the laws of the State of Delaware, United States of America, of 10 Finderne Avenue, Bridgewater, New Jersey 08807, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Our invention relates to starch derivatives for use in paper making, to a method for making paper, using these derivatives and to the paper thus obtained.

As used herein, the term "paper" includes sheet-like masses and molded products made from fibrous cellulosic materials, which may be derived from natural sources as well as from synthetics such as polyamides, polyesters and polyacrylic resins, as well as from mineral fibers such as asbestos and glass fibers. Also included are papers made from combinations of cellulosic and synthetic materials. Paperboard is, of course, also included, within the broad term "paper".

It has been known to add various materials, including starch, to the pulp, or stock, during the papermaking process, prior to the formation of the sheet. The purpose of such additives has been mainly to promote fiber bonding and to facilitate the formation of stronger paper.

Furthermore, in the case of those papers which contain added pigments, such for example as titanium dioxide, it has been known to add materials to the pulp, or stock, for the specific purpose of retaining a greater proportion of such pigments in the paper (rather than have them drain off in the water that is removed during the formation of the sheet). Such additives are often referred to as "pigment retention agents".

One of the serious problems heretofore encountered in paper manufacture has been that additives employed for binding and strengthening the paper had insufficient effect in improving pigment retention, or in many cases actually decreasing the amount of pigment retained by the paper. Similarly, those additives which were most effective as pigment retention agents had no effect in strengthening the ultimate paper sheet, or in some cases actually drastically weakened it.

The aminoalkyl starch ethers described in U.S. Patent No. 2,813,093 and employed in the papermaking process of U.S. Patent No. 2,935,436 have brought about improvements in both paper strength and pigment retention. However, the search for greater improvements has continued, with the particular objective of providing an additive that would be effective at a low pH range in the presence of aluminum salts, regardless of the hardness of the water which is employed in the pulp and in cooking the starch.

It has been proposed to use starch phosphates as pigment retention agents, and their effectiveness has been noticeable with paper stock containing low to moderate concentrations of alum. At higher alum concentrations, however, the effectiveness of starch phosphates declines, due to reasons not readily understood. Possibly this is because the phosphate groups function as weak acids, which are incapable of providing desired pigment retention and of increasing paper strength in the presence of alum concentrations greater than 4 per cent, by weight, of the dry pulp. Thus, starch phosphates (e.g., di- and tri- alkyl aminoalkyl starch

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- phosphates), like other anionic starch derivatives of the prior art which are effective at lower concentrations of alum, are inferior at higher alum concentrations.
- At low alum concentrations, some pigment retention performance improvements can be obtained by introducing carboxyl groups such as carboxymethyl groups or half ester groups (e.g. succinate groups or maleate groups) in starch amine alkyl ethers or native starches.
- However, the search for greater improvements has continued, with the particular objective of providing an additive that would be effective at the higher alum concentrations often found in the paper industry, particularly in connection with the increasing utilization of recycled paper.
- Thus, it is the object of this invention to provide novel starch products which are useful in the manufacturing of paper having high alum acidity.
- According to one aspect of the present invention there is provided a starch derivative of a starch base having a water fluidity of from 4 to 40, said starch derivative containing chemically introduced sulfo-succinate groups in a degree of substitution of at least 0.008 and cationogenic or cationic nitrogen-containing substituent groups selected from sulfonium, phosphonium, primary amine, secondary amine, tertiary amine and quaternary ammonium groups, in a degree of substitution of from 0.005 to 1.50.
- In addition to the foregoing nitrogen/cationic groups and sulfo-succinate groups, the starch derivatives may also contain phosphate groups as described hereinafter, hydroxypropyl groups, acetate groups or other substituent groups in amounts permitting granular starch character and increasing solubility.
- As the cationogenic or cationic substituent in our starch additive, we prefer a tertiary amine ether or quaternary ammonium ether group. However, other cationogenic or cationic groups are operable, as for example, primary and secondary amine groups, sulfonium and phosphonium groups attached by ether or ester linkages.
- The preparation of the aminoalkyl ethers of starch, wherein the starch derivative contains tertiary amine groups, is described in U.S. Patent No. 2,813,093. Similarly, sulfonium and phosphonium derivatives of starch are described in U.S. Patent Nos. 2,989,520 and 3,077,469, respectively.
- It is known that quaternary ammonium groups may be introduced into the starch molecule by suitable treatment of the tertiary aminoalkyl ether of starch, as described, for example, in U.S. 2,813,093 or quaternary groups may be introduced directly into the starch molecule as, for example, by treatment with the reaction product of an epihalohydrin and a tertiary amine or tertiary amine salt.
- Also, as stated, the starch derivatives to be suitable as an additive to the paper pulp in the process of our invention, must contain sulfo-succinate ester groups. It should be mentioned that, for the purpose of our invention, the sulfo-succination of the starch, i.e., the chemical introduction of the sulfo-succinate groups to the anhydroglucose units, is to be carried out after the starch has been modified with the nitrogen containing cationogenic or cationic groups and, preferably, after it has been converted.
- Various techniques for sulfo-succinating the starch base are well known to those skilled in the art. For example, U.S. Patent No. 2,825,727 discloses a method for treating ethylenically unsaturated starch derivatives prepared according to the method described in U.S. Patent Nos. 2,461,139 and 2,668,156 with bisulfite.
- The starch bases suitable for the practice of our invention must be in the intact granular form and must have or be converted to a water fluidity of at least 4 but no greater than 40. Hence, among the suitable starch bases are included those in their ungelatinized form, which may be derived from any plant source such as corn, rice, tapioca, sago, waxy mazie, sorghum, potato, sweet potato, wheat, high amylose corn or the like. The particular starch chosen may be converted to its fluidity or thin-boiling form at any stage prior to sulfo-succination, using any suitable method of degradation such as thermal treatment in the presence of sodium phosphate with an amylase on granular starch, or mild oxidative conversion, or mild acid hydrolysis or controlled enzyme conversion. Therefore, since the necessary conversion of the starch to a water fluidity within the prescribed range may be carried out before or after modification with the cationic groups, the selection of the sequence prior to sulfo-succination is left to the practitioner. We have also found that the phosphate ester groups, such as found in potato starch, or the introduction of such groups into corn starch by heat reacting with phosphate salts make the starch

- suitable for introduction of the sulfo-succinate groups without converting. The degree of substitution (D.S.) of the phosphate groups may range from 0.003 to 0.01.
- We have found that the starch derivatives suitable for use in the process of this invention should be substituted with cationogenic/cationic groups to such an extent that their degree of substitution (D.S.), i.e. the average number of cationogenic/cationic groups per anhydroglucose unit of the starch molecule ranges from 0.005 to 1.50, generally at least 0.01, and preferably from 0.02 to 0.04. At higher D.S. ranges, it is necessary to protect the granule structure by means known to those skilled in the art.
- Any of the foregoing types of substituent groups may be utilized separately or in combination with any of the other useful nitrogen containing groups or with sulfonium or phosphonium groups, so long as the total D.S. does not exceed 1.50.
- The quantity of the sulfo-succinate ester groups chemically bound to the starch molecule, and more specifically to the anhydroglucose unit, is important because it affects the pigment retention in presence of alum concentrations higher than about 4%. Although the presence of very small amounts of the sulfo-succinate ester groups will demonstrate improvements (e.g., 0.008 moles per mole of anhydroglucose unit), 0.02 or more is the preferred amount.
- Since the aim of this invention is not to provide a balanced performance at various pHs, but improved performance in the presence of high concentrations of alum e.g. above 4% by weight of the dry pulp, the ratio of the anionic groups to cationogenic or cationic groups is of lesser importance. However in some embodiments the presence of cationogenic or cationic groups has been found noticeably to improve retention and strength at lower concentrations of alum.
- As previously mentioned, it is also possible to employ in our process starch derivatives containing other substituent groups beside the required cationogenic/cationic and sulfo-succinate groups.
- The technique for phosphorylating a starch base is known to those skilled in the art. Thus, U.S. Patent Nos. 2,824,870, 2,884,412 and 2,961,440 disclose various phosphorylation techniques consisting, essentially, of heat reacting starch impregnated with a phosphate salt of an alkali metal, within a prescribed pH range. For the purpose of our invention, the phosphorylations are limited to reactions of starch with any phosphorylating agent yielding orthophosphate monoester groups, i.e. mono-starch phosphates.
- A representative method for carrying out a suitable phosphorylation would be similar to that described in assignee's U.S. Patent No. 3,459,632.
- The preparations of the phosphonium and sulfonium starch derivatives are described in U.S. Patent Nos. 3,077,469 and 2,989,520, respectively.
- It will be apparent that various other optional cationogenic or cationic substituents may similarly be linked to a common anhydroglucose unit, it being remembered that in carrying out our process, not only is it imperative that the starch base be converted to a water fluidity of from 4 to 40 but the synergistic combination of the specified substituent groups must be present within the prescribed range.
- The herein described starch derivatives are used mainly as beater additives, although their addition may occur at any point in the paper-making process prior to the ultimate conversion of the wet pulp into a dry web or sheet. Thus, for example, they may be added to the pulp while the latter is in the headbox, beater, hydropulper or stock chest.
- The pigment retention and strength agents of our invention may, of course, be effectively used for addition to pulp prepared from any types of cellulosic fibers, synthetic fibers, or combinations. Among the cellulosic materials which may be used are bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical, chemiground wood, ground wood or any combination of these fibers. Fibers of the viscose rayon or regenerated cellulose type may also be used if desired.
- Any desired inert mineral fillers may be added to the pulp which is to be modified with our novel starch derivatives. Such materials include clay, titanium dioxide, talc, calcium carbonate, calcium sulfate and diatomaceous earths. Rosin or synthetic internal sizer may also be present, if desired.
- With respect to the proportion of the starch derivative to be incorporated with the paper pulp, we have found that this may vary in accordance with the particular pulp involved. In general, we prefer to use about 0.05% to 2.0% of the starch derivative, based on the dry weight of the pulp. Within this preferred range

the precise amount which is used will depend upon the type of pulp being used, the specific operating conditions, and the particular end use for which the paper is intended. The use of amounts of starch derivative greater than 2%, on the dry weight of the pulp, is not precluded, but is ordinarily unnecessary in order to achieve the desired improvements. When added in the proper concentrations, our starch derivatives serve to increase pigment retention and paper strength, while providing the finished sheet with improved resistance to folding, picking and scuffing.

The starch derivatives employed in preferred embodiments of our process contain cationic aminoalkyl ether or quaternary ammonium groups and sulfo-succinate ester groups in carefully balanced ratios, yielding a combination of charge which come into play alternatively under varying conditions of application, such as varying alum concentrations or water hardness. Further, and surprisingly the interaction of the sulfo-succinate cationogenic and cationic groups generally leads to a well-balanced performance of the starch derivatives over a wide range of water hardness and alum concentration. This surprising synergistic effect makes our additives particularly useful within the wide range of operating conditions existing in the papermaking art utilizing the presence of more than 4 per cent by weight alum in the dry pulp.

The following examples will further illustrate the invention. Unless otherwise stated, all parts are by weight.

#### EXAMPLE I.

This example illustrates the preparation of a typical alkylamine, phosphate and sulfo-succinate starch derivative suitable for the practice of this invention.

The method outlined in Example I of U.S. Patent No. 3,459,632 was utilized to modify a quantity of granular corn starch with tertiary amine and phosphate groups. The resulting starch derivatives had about 0.3 per cent, by weight, of nitrogen and, on the same basis, about 0.08 per cent of phosphorous and a water fluidity in the range 8 to 20. It is to be noted, since the starch base was phosphorylated, i.e., modified with phosphate groups, conversion of the same was not necessary. The D.S. of the phosphate groups was about 0.008.

Part I: To chemically introduce the sulfo-succinates to a portion of the modified starch described above, about one hundred parts of said modified starch was suspended in about 125 parts of tap water. The suspension was stirred, and the pH of the resulting slurry was adjusted to and maintained at 7.2 by the addition of dilute sodium hydroxide solution, while 1 part of maleic anhydride was added in small increments. Then the mixture was allowed to react, as agitation was continued, over a period of about one hour to ensure complete esterification. Thereafter about 6 parts of sodium metabisulfite were slowly added to the reaction vessel. This mixture was then allowed to react, under agitation and at ambient temperature, for about 16 hours. After the reaction was completed, the pH level of the system was adjusted to 5.5 by the addition of hydrochloric acid. The reaction product was then recovered by filtration, washed essentially free of salts with tap water, and dried. The resulting product had a D.S. of about 0.028 with respect to the tertiary amine groups and a D.S. of about 0.01 with respect to the sulfo-succinate groups. A portion of the dried starch product was then used as an additive in the preparation of paper and subsequently tested for its pigment retention properties as set forth below.

Part II: Each of three portions of the starch derivative described above were added to a bleached sulfite pulp which contained a varied amount of paper alum, i.e., aluminum sulfate. Said portions of starch derivative were each added to the paper-making pulp at a concentration of 0.25 per cent, based on the weight of the dry pulp. The three pulps respectively contained 4.0, 11.0, and 15.0 per cent, by weight, of alum, based on the total system. In each case, the pigment retention value of the test paper stock and those of a blank and a control were determined by first preparing paper sheets on the Williams Standard Sheet Mold and then testing for the per cent of titanium dioxide ( $TiO_2$ ) retained by the method described in TAPPI Standard T413-ts-66. The blank merely consisted of the paper-making stock without any additive, and said control comprised a commercially available pulp having therein a tertiary amine phosphate starch derivative. The test results are presented below.

	<u>Material Tested</u>	<u>Additive</u>	% TiO <sub>2</sub> R tention in pres nce of foll wing amounts of Alum*		
			4.0	11.0	15.0
5	Test Sample	Tertiary Amine phosphate sulfo-succinate starch	72	73	72
	Blank		43	37	42
	Control	Tertiary Amine phosphate	72	56	52

\*Based on the per cent, by weight, of the dry pulp.

10      The data summarized above indicate the improved pigment retention obtained by the use of the novel starch products of the invention.      10

#### EXAMPLE II.

15      This example further illustrates the increased pigment retention effectiveness of the starch derivatives of this invention, using a relatively greater amount of sulfo-succinate groups.      15

20      The steps set forth in Part I of Example I were repeated, except two parts of maleic anhydride were used to esterify the modified corn starch prior to sulfonation. The resulting starch derivatives had D.S. values of 0.026 and 0.03 for the tertiary amino groups and the sulfo-succinate groups, respectively. When a portion of this starch product was tested in the manner described in Part II of Example I, it displayed pigment retention values comparable to those of the test sample in said example.      20

#### EXAMPLE III

25      This example illustrates the increased pigment retention effectiveness of the starch derivatives of this invention, using a relatively greater amount of succinating agent with a slightly lesser amount of sulfonating agent.      25

30      The method outlined in Example I of U.S. Patent No. 3,459,632 was used to modify a quantity of potato starch with tertiary amine groups. The pH of the slurry after reaction was adjusted to 3.0 by the addition of hydrochloric acid. Thereafter the reaction product, which had a water fluidity of 8.0, was recovered by filtration, washed free of salts, and then reacted with two parts of maleic anhydride and four parts of sodium metabisulfite in the manner described in part I of Example I to form tertiary amino, sulfo-succinate starch derivatives. The resulting product had D.S. values of 0.03 and 0.02 for the tertiary amino group and the sulfo-succinate group, respectively. Upon being tested by the method outlined in Part II of Example I, this derivative showed pigment retention values, in the presence of the varied higher amounts of alum, of 79%, 75%, and 76%, respectively.      35

#### EXAMPLE IV.

40      This example illustrates the preparation of a sulfo-succinate derivative of a cyclic tertiary amine starch ether for use as a pigment retention additive for paper-making stock.      40

45      To make the additive described above, 100 parts of potato starch were slowly stirred into 125 parts of water. The suspension thus formed was then reacted with 1 part of betachloroethyl piperidine HCl, in the presence of 0.5 parts of calcium oxide, over a period of 16 hours at ambient temperature. The pH of the resulting slurry was then adjusted to 3.0 by the addition of hydrochloric acid. Thereafter the reaction product which had a water fluidity of 8.0, was recovered by filtration, washed free of salts, and then reacted with 2 parts of maleic anhydride and 4 parts of sodium metabisulfite in the manner described in Part I of Example I to form the tertiary amino, sulfo-succinate starch derivatives. The respective pigment retention values of this derivative, determined according to the procedure set forth in Part I of Example I, were 80, 76, and 76. The product had D.S. values of 0.01 and 0.02 for the tertiary amino group and the sulfo-succinate group, respectively. These results reflect the ability of a starch derivative, wherein the starch base contains naturally occurring phosphorous, to be used as a paper additive in accordance with the invention. Furthermore, these results illustrate that, when      50

such a starch base is employed, the conversion step prior to sulfo-succination may be omitted.

#### EXAMPLE V.

This example illustrates the preparation of a quaternary ammonium, sulfo-succinate starch derivative which is useful in the practice of this invention. To make the starch derivative described above, 100 parts of corn starch were slowly stirred into 130 parts of tap water containing 4 parts of calcium hydroxide, the corn starch having a water fluidity of about 8. The suspension thus formed was then reacted with 3 parts of trimethyl-2-hydroxy-3-chloropropyl ammonium chloride, under agitation and at ambient temperature over a period of about 16 hours. The pH of the resulting slurry was then adjusted to 3.0 by the addition of hydrochloric acid. Thereafter the reaction product was recovered by filtration, washed essentially free of salts, and then suspended in about 140 parts of water. Two parts of maleic anhydride and then 5 parts of sodium metabisulfite were reacted with the quaternary amine modified starch of the suspension, in the manner described in Part I of Example I. This modified starch product had a quaternary ammonium group D.S. of 0.01 and a sulfo-succinate group D.S. of 0.03. Then each of three equal portions of the thusly prepared quaternary ammonium, sulfo-succinate starch derivative were added to a particular slurry of a paper-making pulp which contained a varied amount of alum. The three pulps respectively contained 0.0, 4.0 and 11.0 per cent, by weight of alum, based on the total weight of the particular mixture. The portions of the starch derivative were each added at a concentration of 0.25 per cent by weight, based on the weight of the dry pulp. The pigment retention value of each of the respective paper stocks obtained from the aforesaid three test pulps and those of a blank and a commercially available control were determined by the method set forth in Part II of Example I. The paper-making stock in the case of the blank and the control were similar to those respectively employed in Part II of Example I. The results are presented below.

	<u>Material Tested</u>	% TiO <sub>2</sub> Retention in presence of following amounts of Alum*			30
		0.0	4.0	11.0	
	Test Sample	13	77	73	
	Blank	8	50	45	
35	Control	41	82	64	35

\*Based on the per cent, by weight, of the dry pulp.

The results presented above indicate that the quaternary ammonium, sulfo-succinate starch, derivatives prepared in accordance with this invention are particularly useful in the manufacturing of paper wherein the paper-making stock contains pulp which has a relatively high alum content.

#### EXAMPLE VI.

This example illustrates the increased pigment retention effectiveness of the starch derivatives of this invention, using an alkylamino phosphate, sulfo-succinate starch derivative of which the starch base has been converted by varied acid treatments. To make each of four test sample additives, a tertiary amino phosphate corn starch was prepared by the method taught in Example I of assignee's U.S. Patent 3,459,632, converted to WF (water fluidity) levels ranging from about 8 to 35 by treatment with a varied amount of hydrochloric acid, and then further modified with sulfo-succinate groups. The acid conversions were carried out at 52.5°C. over a period of about 16 hours. After each reaction was completed, the resulting mixture was neutralized by the addition of dilute NaOH, and the tertiary amino phosphate starch was recovered by filtration and then washed. Thereafter about 150 parts of each product was further modified by treatment with 2 parts of maleic anhydride and 4 parts of sodium metabisulfite. The D.S. value for the tertiary amine group and for the sulfo-succinate group were 0.03 to 0.02, respectively. The

5 pigment retention values for the four test samples and those of the blank and the three varied controls were determined by the method described in Part II of Example I. The varied amount of hydrochloric acid used to convert the starch, the varied amounts of alum employed in the pulp, and the respective test results obtained with the various materials tested are presented in the following table.

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	<u>Material Tested</u>	<u>HCl (Parts)</u>	% TiO <sub>2</sub> Retention in presence of following amounts of Alum*		10
			4.0	11.0	
10	Sample A	Tertiary Amine phosphate sulfo-succinate starch	0.25	79	75
	Sample B	(Same as that used in Sample A)	0.5	81	90
15	Sample C	" " " " "	0.75	73	75
	Sample D	" " " " "	1.0	74	76
	Control	Tertiary Amine Starch	—	56	46
	#1		—		
	Control #2	Tertiary Amine, phosphate starch	—	79	52
20	Control #	Tertiary Amine, sulfo- succinate of a non- converted starch	—	60	59
	Blank	—	—	44	45

\*Based on per cent, by weight, of the dry pulp.

25 The data summarized above indicate that in order to obtain improved pigment retention, it is imperative that the base starch be converted as well as modified with the nitrogen containing groups and the sulfo-succinate groups.

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#### EXAMPLE VII.

30 This examples illustrates the usefulness of a starch derivative of this invention, as an additive for paper-making pulp, wherein the base starch of the derivative has been converted prior to modification. Also, this example further illustrates the crucial nature of the conversion step in the preparation of the paper-making additives of this invention.

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35 A test sample additive was prepared by treating a quantity of corn starch with 0.5% HCl to a WF of about 10, then diethylamino ethylating the starch by the method taught in part A of Example I of U.S. Patent 3,459,632, and thereafter further modifying the starch with sulfo-succinate groups by the method outlined in Part I of Example I. The resulting starch product had a diethylamino ethyl group D.S. of 0.03 and a sulfo-succinate group D.S. of about 0.02. This test sample additive and four varied controls were added to bleached pulp at concentrations of 40 0.25% based on the weight of the dry pulp. Pigment retention values were determined for each additive and a blank at varied levels of alum as described in Part II of Example I. The identification of the controls and their respective descriptions were as follows:

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40 Control No. 1 — Corn starch modified with sulfo-succinate groups (D.S. of about 0.02) by the method set forth in Part I of Example I.

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45 Control No. 2 — Corn starch modified with diethylamino ethyl groups (D.S. of about 0.03) by the method set forth in Part A of Example I of U.S. Patent 3,459,632.

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Control No. 3 — Corn starch modified with both diethylamino ethyl groups (D.S. of about 0.03) and sulfo-succinate groups (D.S. of about 0.02) by the respective methods mentioned above.

5 Control No. 4 — Corn starch which has been acid-converted in the same manner as the starch base of the test sample herein and thereafter modified with diethylamino ethyl groups (D.S. of about 0.03) by the method taught in Part IA of U.S. Patent 3,459,632.

10 The results of the pigment retention determinations for the above-described test sample additive, the four control additives, and the blank are presented in the following table.

15	<u>Material Tested</u>	% TiO <sub>2</sub> Retention in presence of following amounts of Alum*	
		4.0	11.0
	Test Sample	69	71
	Control No. 1	62	59
	Control No. 2	56	46
	Control No. 3	60	59
20	Control No. 4	52	46
	Blank (pulp without an additive)		

\*Based on per cent, by weight, of the dry pulp.

25 The data obtained for the test sample and control No. 3 in the above table indicate an outstanding pigment retention performance for the starch derivatives in accordance with the invention, the starch base having been converted prior to being esterified.

#### EXAMPLE VIII.

30 This example further illustrates the pigment retention properties of an aminoalkylate, sulfo-succinate starch derivatives of which the starch base has been acid-converted prior to esterification with a varied amount of maleic anhydride.

35 To make each of three test sample additives, a quantity of tertiary amine corn starch was prepared by the method taught in Example I of U.S. Patent 3,459,632 and then converted to a WF of about 8 by treatment with 0.5 parts of HCl. The resulting, converted starch product was then divided into three equal portions. Each of the portions of the starch product was esterified with a varied amount of maleic anhydride and thereafter sulfonated by reaction with four parts of sodium metabisulfite. The acid conversions were carried out at 52.5°C. over a period of 16 hours. Each of the tertiary amino, sulfo-succinate starch derivatives thus obtained was recovered by filtration, washed, and dried. These test sample additives, two commercially available paper-making starch additives, and a blank were tested for their pigment retention properties by the method described in Part II of Example I. The amount of maleic anhydride used in the preparation of each of the test sample additives and the corresponding tertiary amino group to sulfo-succinate group ratio therein, the descriptions of the two controls, and all test results are presented in the following table.

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			D.S. of sulfo-succinate groups	D.S. of tertiary-amino group	TiO <sub>2</sub> Retention in presence of Alum		
					4.0	11.0	
5	Sample E	Tertiary amine sulfo-succinate starch	0.01	0.03	75	74	5
10	Sample F	(Same as that used in Sample E)	0.02	0.03	76	74	
15	Sample G	(Same as that used in Sample E)	0.03	0.03	77	77	10
20	Control #1	Tertiary amino-alkyl ether of starch (prepared by the procedure described in Ex. 1 of U.S. 2,813,093)			55	48	
25	Control #2	Phosphorylated tertiary amino-alkyl ether of starch (prepared by the procedure described in Ex. 1 of U.S. 3,459,632 (D.S. of about 0.03))			75	56	15
	Blank				41	43	20
30		The data summarized hereinabove clearly indicate the improved pigment retention obtained by the use of the test sample additives. It further indicates that the extremely high percentages of pigment were consistently retained in the presence of greater amounts of alum, only where the test sample additives were used.					30

#### EXAMPLE IX.

This example illustrates the usefulness of thin boiling starches in the preparation of starch paper additives in accordance with the invention.

To make each of the two test sample additives, the procedural steps set forth in Example VII were repeated, except a thin boiling waxy maize which had a particular Water Fluidity (WF) was used in each case. Each of the resulting starch derivatives had a tertiary amine group D.S. of about 0.03 and a sulfo-succinate group D.S. of about 0.03. The two test sample additives and a blank were then tested in the manner described in Part II of Example I. The WF's of the waxy maize used to prepare the additives and the pigment retention determinations are presented below.

45	<u>Material Tested</u>	% TiO <sub>2</sub> Retained in the presence of the following amounts of Alum			45
		WF	4.0 parts	11.0 parts	
	Test Sample H	24	72	79	
	Test Sample I	36	68	76	
	Blank	—	43	45	

The data summarized above indicate the improved pigment retention obtained by the use of the test sample additives prepared with thin boiling starch bases. It further indicates the ability of the test sample additives to consistently retain greater amounts of pigment despite a substantial increase in the amount of alum used.

## **EXAMPLE X.**

This example illustrates the usefulness of a starch derivative as a paper additive, wherein the starch base has been simultaneously converted by homolytic oxidation and etherified with aminoalkyl groups prior to esterification.

In order to make a starch derivative in the above described manner, 100 parts of corn starch were suspended in about 125 parts of tap water at about 40°C. The pH of the resulting slurry was adjusted to 11.2 by the addition of dilute sodium hydroxide. Then 3 parts of diethylamino-ethylchloride — HCl, 0.5 parts of calcium hydroxide, and 0.5 parts of 30% aqueous hydrogen peroxide were added to the slurry. While the pH was maintained at the aforesaid level, the mixture was agitated for about 17 hours. Thereafter, the pH of the reaction mixture was adjusted to 3.0 by the addition of dilute hydrochloric acid, and the reaction product was recovered by filtration and thoroughly washed. It was determined that the converted starch had a WF of about 7. This intermediate base was then suspended in water at a ratio of 1.0 part per 1.3 parts of water, reacted with 2.0 parts of maleic anhydride and thereafter with 4.0 parts of sodium metabisulfite. The thusly prepared diethylaminoethyl, sulfo-succinate starch derivative was recovered in the manner described in Part I of Example I. This starch derivative had diethylaminoethyl group and sulfo-succinate group D.S. values of 0.03 and 0.02, respectively. Then this derivative, a commercially available control and a blank were tested for their pigment retention properties by the method outlined in Part II of Example I. The control consisted of a standard paper-making stock containing an aminoalkyl etherified and phosphorylated starch additive, and the blank merely consisted of the paper-making stock. The test results were as follows:

30	% TiO <sub>2</sub> Retention in presence of following parts of Alum	
<u>Material Tested</u>	4.0	11.0
Test Sample	74	70
Control	71	61
Blank	43	45

The data summarized above indicate the improved pigment retention consistently obtained by the use of the test sample additive in the presence of high as well as low amounts of alum.

### EXAMPLE XI.

**EXAMPLE XI.**  
This example further illustrates the usefulness of a starch derivative as a paper additive, wherein the starch base has been simultaneously converted by oxidation and etherified with aminoalkyl groups prior to esterification.

The procedural steps of Example X were repeated, except only 0.1 parts of 30% aqueous hydrogen peroxide was used without any calcium hydroxide, and the etherification was carried out over a period of only 5.75 hours. When tested by the method described in Part II of Example I hereinabove, this diethylaminoethyl (D.S. of about 0.03) sulfo-succinate (D.S. of about 0.02) starch derivative showed pigment retention values comparable to those of the test sample in Example X.

### EXAMPLE XII.

This example compares the burst strength which is obtained with the use of additives in accordance with the invention with the strength of either untreated sheets or sheets treated with a conventional diethylamino ethyl ether of a phosphorylated starch.

55 A quantity of a diethylamino ethyl ether and sulfo-succinate derivative, having a formulation similar to that of the test sample in Example VI, was prepared according to the general procedure set forth in Part I of Example I.

With agitation, two test sample paper-making stocks, H and I, were prepared by adding a varied amount of the above-described starch additives to an unbleached pulp containing 11.0 parts of alum, based on the weight of the dry pulp. The starch additive additions were made, to dilute the paper stock, at concentrations of 0.5 to 1.5 per cent, respectively, based on the dry weight of the pulp. Sheets were then prepared from each of the pulp stocks on a Williams Standard Sheet Mold.

The strength of these sheets was determined using the Mullen tester according to procedures set forth in TAPPI Standards T403, ts-63. In this apparatus a sheet of paper is clamped between two ring shaped platens, thus leaving an exposed circular surface of paper under which there is an inflatable rubber diaphragm. As air is pumped into this diaphragm it expands and comes into contact with the exposed surface of the paper. Note is made of the pressure, in p.s.i., at which the diaphragm caused the paper to burst. The Mullen factor is then calculated by dividing the latter figure by the basis weight of the paper, a higher Mullen factor thus indicating a stronger paper.

Using the same paper-making procedure as described above, comparable sheets were prepared with, in one case, a control comprised of the standard pulp stock having a conventional diethylamino ethyl ether of starch additive therein and, in another case, the standard pulp stock without an additive. The test results in terms of Mullen values were as follows:

	<u>Material Tested</u>	<u>% Additive</u>	<u>Mullen</u>	<u>Mullen Factor</u>	
	Test Sample H	0.5	77.6	1.44	
	Test Sample I	1.5	92.3	1.59	
25	Control	0.5	66.8	1.32	25
	Control	1.5	76.8	1.45	
	Blank	—	60.7	1.12	

The data presented above show the improved bursting strength of the sheets obtained with pulp containing the additive in accordance with the invention.

Although it will be noted that in some cases the starch derivative in accordance with the invention, containing both the cationic or cationogenic aminoalkyl ether groups and the sulfo-succinate groups, is not significantly more effective at the low concentrations of alum than a starch derivative which contains aminoalkyl ether groups in combination with only phosphate groups, the important factor is that the derivative in accordance with the invention is effective as a pigment retention and strength additive in the presence of higher as well as low concentrations of alum.

#### WHAT WE CLAIM IS:—

1. A starch derivative of a starch base having a water fluidity of from 4 to 40, said starch derivative containing chemically introduced sulfo-succinate groups in a degree of substitution of at least 0.008 and cationogenic or cationic nitrogen-containing substituent groups selected from sulfonium, phosphonium, primary amine, secondary amine, tertiary amine and quaternary ammonium groups, in a degree of substitution of from 0.005 to 1.50.
2. A starch derivative according to claim 1, wherein said substituent groups are diethyl aminoethyl groups.
3. A starch derivative according to claim 2, wherein the starch base is corn starch, and the degree of substitution of said diethyl aminoethyl groups in said starch derivative is 0.02 to 0.04.
4. A method of making paper which comprises adding to the stock, at any stage prior to forming a web, a starch derivative of a starch base as defined in anyone of claims 1 to 3.
5. A paper containing alum and having dispersed therein a starch derivative of a starch base as defined in anyone of claims 1 to 3.

6. A starch derivative according to claim 1, substantially as herein described with reference to anyone of Examples I to XI.

7. A method of making paper according to claim 4, substantially as herein described, with reference to anyone of Examples I to XII.

8. A paper according to claim 5, substantially as herein described with reference to anyone of Examples I to XII.

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